<Division of Materials Chemistry>Polymer Controlled Synthesis

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– Polymer Controlled Synthesis –

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AROUA, Safwan — Eidgenössische Technische Hochschule Zürich, Switzerland, 16 September–15 October
GROS, Alice Yukiko — Ecole Centrale de Nantes, France, 30 October–25 November

Scope of Research

Our research focuses on creation of new organic molecules which would become key reagents and materials for future science and technologies. Furthermore, we have been developing new organic and polymeric materials based on our tailor-made molecules. One such topic is the development of new living radical polymerization method utilizing heavier heteroatom compounds as controlling agents. The other topic is the synthesis of cycloparaphenylenes, hoop-shaped π-conjugated molecules, based on new synthetic strategy. We also study various polymer condensed states by both static and dynamic methods to understand the relation of physical properties and structures.

KEYWORDS

Organic Synthesis
Polymer Synthesis
Living Radical Polymerization
Polymer Properties
Curved π-Conjugated Molecules

Selected Publications

Iwamoto, T.; Kayahara, E.; Yasuda, N.; Suzuki, T.; Yamago, S., "Synthesis, Characterization, and Properties of [4]Cyclo-2,7-pyrenylene: Effect of Cyclic Structure on the Electronic Properties of Pyrene Oligomers", *Angew. Chem. Int. Ed*., **53,** 6430-6434 (2014).
Kayahara, E.; Patel, V. K.; Yamago, S., "Synthesis and Characterization of [5]Cycloparaphenylene", *J. Am. Chem. Soc*., **136,** 2284-2287 (2014).
Nakamura, Y.; Arima, T.; Yamago, S., "Modular Synthesis of Mid-Chain Functionalized Polymers by Photoinduced Diene- and Styrene-Assisted Radical Coupling Reaction of Polymer-End Radicals", *Macromolecules*, **47,** 582-588 (2014).
Nakamura, Y.; Nakanishi, K.; Yamago, S.; Tsujii, Y.; Takahashi, K.; Morinaga, T.; Sato, T., "Controlled Polymerization of a Protic Ionic Liquid Monomer by ARGET ATRP and TERP", *Macromol. Rapid Commun*., **35,** 642-648 (2014).
Kayahara, E.; Iwamoto, T.; Takaya, H.; Suzuki, T.; Fujitsuka, M.; Majima, T.; Yasuda, N.; Matsuyama, N.; Seki, S.; Yamago, S., Synthesis and Physical Properties of a Ball-like Three-dimensional π-conjugated Molecule, *Nature Commun*., **4,** 2694 (2013).

Synthesis and Characterization of [5]Cycloparaphenylene

Considerable interest has recently been focused on hoop-shaped π-conjugated molecules because of their great potential in molecular electronics. In particular, cycloparaphenylenes (CPPs) which consist of phenylene units that are para-linked in a cyclic manner, have attracted increasing attention in this area for not only their aesthetic structure having radially extended unique π orbitals originating from the curvature but also their applications in electronic and optoelectronic materials. However, the synthesis of CPPs has been a significant challenge because of the difficulty in constructing the highly strained cyclic structure. We achieved the synthesis of highly strained [5]CPP, a structural unit of the periphery of C_{60} and the shortest possible structural constituent of the sidewall of a (5,5) carbon nanotube, in nine steps in 17% overall yield. The synthesis relied on metal-mediated ring closure of a triethylsilyl (TES)-protected masked precursor followed by removal of the TES groups and subsequent reductive aromatization. UV−vis and electrochemical studies revealed that the HOMO−LUMO gap of [5]CPP is narrow and is comparable to that of C_{60}, as predicted by theoretical calculations. The results suggest that [5]CPP should be an excellent lead compound for molecular electronics.

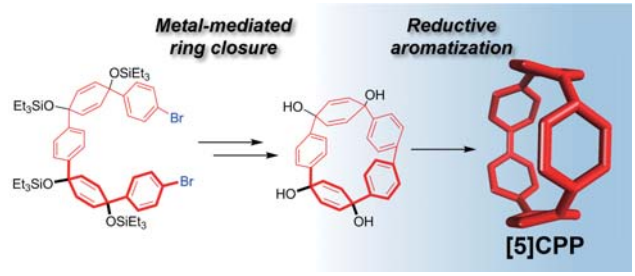

Figure 1. Synthesis of [5]CPP.

Modular Synthesis of Mid-Chain-Functionalized Polymers by Photoinduced Diene- and Styrene-Assisted Radical Coupling Reaction of Polymer-End Radicals

An array of precisely located functional groups in natural macromolecules, such as nucleotides and proteins, plays a pivotal role in their well-defined three-dimensional structure and numerous functions. Therefore, controlling the position and number of reactive functional groups in a structurally well-defined synthetic polymer has been an important challenge in order to create novel functional polymer materials with enhanced or new properties. Photo-irradiation of structurally well-defined "living" polymers prepared by organotellurium-mediated living radical polymerization in the presence of dienes or styrenes induced selective polymer-end coupling reaction with the concomitant insertion of the dienes or styrenes with >90% coupling efficiency. The number of inserted dienes or styrenes could be highly controlled to two molecules when acrylic polymers were used. Therefore, various mid-chain-functionalized polymers with well-controlled molecular and macromolecular structure in terms of their molecular weight, molecular weight distribution, functionality, and position were successfully synthesized by employing functionalized dienes or styrenes. The method was applied to the facile synthesis of mid-chain-functionalized telechelic polymers and a 4-miktoarm star polymer with a well-controlled structure.

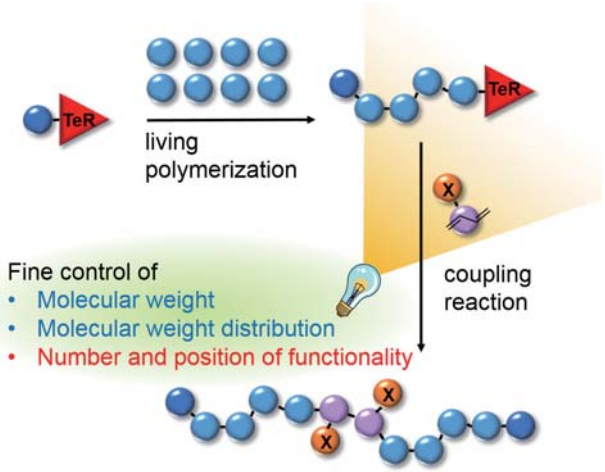

Figure 2. Novel synthetic strategy for mid-chain-functionalized polymers.